Co-sensitization promoted light harvesting for organic dye-sensitized solar cells using unsymmetrical squaraine dye and novel pyrenoimidazole-based dye

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HIGHLIGHTS

- A novel organic dye, 5c, is used with the SQ2 dye for co-sensitizing DSSC.
- The co-sensitized dyes, SQ2/5c, have complementary absorption window.
- Higher efficiencies of the co-sensitized DSSCs are achieved by adding CDCA.
- A high efficiency of 6.70% is achieved for the co-sensitized DSSC under 1 sun.
- The DSSC with the co-sensitized dyes of SQ2/5c shows durability up to 1000 h.

GRAPHICAL ABSTRACT
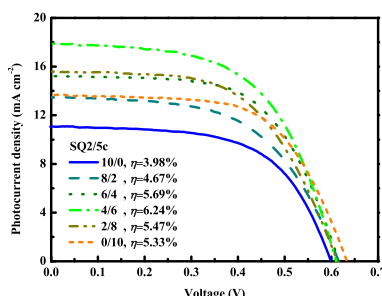
ABSTRACT

The pure organic dyes are investigated recently because of its high extinction coefficient and relatively low cost. In order to enhance the performance of the organic dyes, co-sensitization strategy is applied. The co-sensitization by the absorption of SQ2/5c shows enhanced photovoltaic performance for the pertinent DSSCs, which leads to a broader light harvesting window (400–750 nm) and a higher overall efficiency of 6.24% while the performances of DSSCs with the individual dyes are 5.33% (5c) and 3.98% (SQ2), respectively. Furthermore, the overall efficiency can be further improved to 6.71% with the incorporation of chenodeoxycholic acid (CDCA). In addition, the incident photon-to-current conversion efficiency (IPCE) and UV–visible absorption spectra are also used to explain and support the behavior of the co-sensitized solar cells. The investigation of the long-term stability of the DSSC based on co-sensitization of SQ2/5c dyes with the use of binary ionic liquid is performed. The DSSC with the co-sensitization strategy possesses an unfailing durability up to 1000 h.

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1. Introduction

In the past few years, significant efforts had been devoted into the research fields of dye-sensitized solar cells (DSSCs) [1–3]. The traditional DSSCs are composed of a dye-sensitized TiO_2 photo-anode, redox electrolyte and counter electrode, and have proved themselves as the most promising low-cost alternative substitutions for conventional Si-based solar cells. In these devices, conversion efficiency (η) is achieved by ultra-fast injection of an electron from a photoexcited dye into the conduction band of TiO_2 and subsequently dye regeneration and holes transportation to the counter electrode.

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Numerous efforts had been devoted to the investigation of DSSCs based on Ru(II) polypyridyl complexes in the past decade since an efficiency higher than 7% was demonstrated for a DSSC first in 1991 by Grätzel's group [4] using Ru(II) polypyridyl complexes as a sensitizer (N3 dye). In the past decade, the efficiencies of the DSSCs with N3 [5], N719 [6], and CYC−B11 [7] dyes were improved to 10.4, 11.18, and 11.50%, respectively. Although the Ru(II) dyes has leading performance in conversion efficiency compared to other dyes, higher cost (Ru element) and lower extinction coefficient (usually $< 3 \times 10^4 \, M^{-1} \, cm^{-1}$) has limited the developing potentials of the DSSCs based on Ru(II) dyes. Therefore, the developments of organic dyes have been an attractive topic for DSSCs.

Organic dyes usually have much higher extinction coefficient (usually $> 3 \times 10^4 \, M^{-1} \, cm^{-1}$). Moreover, they can be prepared and purified in a more easy and economical way. Also, with the higher extinction coefficient, applying much thinner TiO_2 thin films for the use of organic dyes than the ruthenium dyes is allowed [8,9]. We can thus minimize the charge transport losses and achieve a better pore filling for solid-state electrolyte of DSSCs.

The organic dyes had attracted considerable attention in recent years [10−13]. Mishra et al. [14] reported some design rules of the organic dyes for the DSSCs, suggesting that the efficiencies of the solar cells not only depend on the molecular structure of the dye, but also depend on its physical properties, such as aggregation and morphology. However, the narrow and sharp light absorption bands and the absence of metal-ligand charge transfer (MLCT) effect had limited the performance of the DSSCs based on pure organic dyes [15]. To achieve higher cell efficiency, a certain sensitizer is needed so as to absorb incident light as much as possible. Unfortunately, currently there is no single organic sensitizer which provides strong absorption in a wide range of wavelengths (400−900 nm) [16]. Therefore, co-sensitization strategy is applied to the organic dyes with complementary absorption spectra to obtain a broader and a more intense absorption band, this increasing the performance of the DSSC [17−19]. In the co-sensitization process, there are two different approaches, normally "molecular cocktail [16]" approach and "band-gap cascade [19]" approach. In the case of co-sensitization with both organic dyes, the improvements are more obvious because the absorption bands are narrower but much sharper than metal-based dyes. Besides, the higher extinction coefficient of the organic dyes can lead to less required amount of the dyes to yield sufficient optical density, which can give sufficient space on the TiO_2 for the attachment of other dyes [8,9]. Several research groups have examined the combination of two or more organic dyes in "molecular cocktails" approach for DSSCs. Sayama et al. [20] revealed that the DSSCs can be sensitized over the entire visible spectrum through the combination of cyanine dyes (cy0, cy1, and cy2), reaching an η value of 2.6%. While the individual η values of the dye coded as cy0, cy1, and cy2 are 0.6, 1.5, and 1.2%, respectively. Kuang et al. [21] dipped the photoanode in the dye cocktail solution of two organic dyes (JK6 and SQ1) for different time spans to reach the co-sensitization effect, and yielded an η value of 6.41% under 100 mW cm^{-2}. Chen et al. [22] mixed three different organic cyanine dyes (merocyanine dye, hemicyanine dye, and squarylium cyanine dye) together in the dye solution before dipping the TiO_2 photoanode into it, and an η value of 6.5% was achieved under 80 mW cm^{-2}.

A novel pyrenoimidazole-based organic dye (5c) was recently reported by our group [23]. The 5c dye absorbs the light between the wavelengths of 360 nm and 520 nm and has a reasonable extinction coefficient of 44,900 M^{-1} cm^{-1} at 464 nm as shown in Table 1. Table 1 also shows the optical properties of the unsymmetrical squaraine dye, SQ2, developed by Geiger et al. [24]. The SQ2 dye mainly absorbs the wavelength of 550−710 nm and possesses a much higher extinction coefficient of 319,000 M^{-1} cm^{-1} at 662 nm. From their

Table 1
Optical properties of the 5c and SQ2 dyes.

|	ε_{max} (M^{-1} cm^{-1})	λ_{max}^{abs} (nm)
SQ2[a]	319,000	662
5c[b]	44,900	464

[a] Ref [24].
[b] Ref [23].

optical properties, the absorption range of the SQ2 dye has spectral characteristics complementary to that of the 5c dye. The chemical structures of SQ2 and 5c are shown in Scheme 1.

In this study, the TiO_2 photoanode of the DSSCs are sensitized with SQ2 and 5c dyes in different volumetric ratios, and the performances of the cells are investigated. Afterward, with the use of pure organic dyes, the cell efficiency of 6.7% is achieved. Incident photon-to-current conversion efficiency (IPCE) curves and UV−visible absorption spectra were employed to substantiate the explanations in this study. Meanwhile, we also studied the at-rest long-term stability for durability of the co-sensitized photoanode. The co-sensitized DSSCs shows uninterrupted overall efficiencies up to 1000 h, which indicates that the photoanodes sensitized with 5c and SQ2 were stable. To the best of our knowledge, this is the highest cell efficiency (6.7%), with long-term stability reported for the co-sensitization of an all-organic dye based DSSC having two organic sensitizers (5c dye and SQ2 dye), when compared to those reported in the previous literatures [20−22].

2. Experimental

2.1. Materials

Lithium iodide (LiI, synthetical grade), iodine (I$_2$, synthetical grade), 3-propyl-1-methyl imidazolium iodide (PMII), and poly(-ethylene glycol) (PEG, M.W. ∼ 20,000) were obtained from Merck; tert-butyl alcohol (tBA, 96%) and 4-tert-butylpyridine (TBP, 96%) were obtained from Acros. Titanium (IV) tetraisopropoxide (TTIP, >98%), 2-methoxyethanol (≥99.5%),1-ethyl-3-methy imidazolium tetrafluoroborate (EMIBF$_4$), and isopropyl alcohol (IPA, 99.5%) were obtained from Aldrich. 3-methoxypropionitrile (MPN, 99%) was
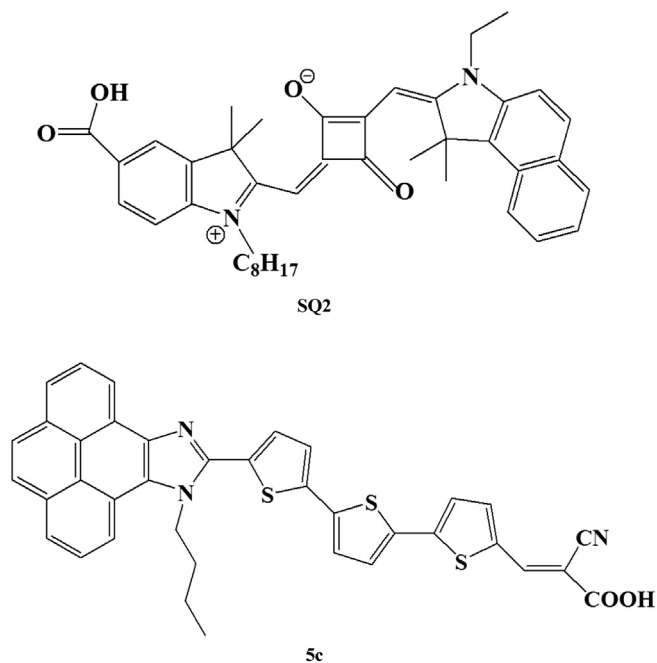
Scheme 1. Molecular structures of 5c and SQ2 dyes.

obtained from Fluka. Acetonitrile (ACN, 99.99%) and nitric acid (*ca.* 65% solution in water) were obtained from J. T. Baker. 1,2-dimethyl-3-propylimidazolium iodide (DMPII) were obtained from Solaronix S.A., Aubonne, Switzerland.

2.2. Preparation of TiO2 pastes

For the TiO_2 colloid solution, the TiO_2 precursor was prepared by sol−gel method as the following processes according to our previous report [25,26]. In brief, TTIP (72 ml) was added to 430 ml of a 0.1 M nitric acid aqueous solution with constant stirring and heated to 88 °C simultaneously for 8 h. When the mixture was cooled down to room temperature, the resultant colloid was transferred to an autoclave (Parr 4540, U.S.A.) and heated at 240 °C for 12 h in order to allow the TiO_2 particles to grow uniformly (*ca.* 20 nm). Consequently, the TiO_2 colloid was concentrated to 10 wt% (with respect to the TiO_2).

The first type of TiO_2 paste (for transparent layer) was prepared by the addition 25 wt% (with respect to the TiO_2) of PEG to the above-mentioned solution in order to control the pore diameters and to prevent the film from cracking during drying. For the second one (for scattering purpose), the first type of TiO_2 paste was incorporated with 50 wt% of light scattering TiO_2 particles (PT-501A, 15 m^2 g^{-1}, 100 nm, 99.74%, Ya Chung Industrial Co. Ltd., Taiwan) to reduce light loss caused by the back scattering.

2.3. Assembly of the DSSCs

A fluorine-doped SnO_2 conducting glass (FTO, 7 Ω sq.$^{-1}$, transmittance in the visible range ≧ 80%, NSG America, Inc., New Jersey, USA) was first cleaned with a neutral cleaner, and then washed with DI-water, acetone, and IPA, sequentially. The conducting surface of the FTO was treated with a solution of TTIP (1 g) in 2-methoxyethanol (99.5%, Sigma−Aldrich, 3 g) for obtaining a good mechanical contact between the conducting glass and TiO_2 film, as well as to isolate the conducting glass surface from the electrolyte.

TiO_2 pastes were coated onto the treated conducting glass by using the doctor blade technique. The coated TiO_2 film was allowed to dry under ambient condition and gradually heated to 450 °C in an oxygen atmosphere, and subsequently sintered at that temperature for 30 min. Before the next coating, the sintered TiO_2 film was treated with UV−ozone for 15 min. The TiO_2 photoanodes of the DSSCs employed in the experiments were composed of a 12 μm thick transparent TiO_2 layer and a scattering layer of 4 μm thickness. The TiO_2 thin film was maintained with an active area of 0.4×0.4 cm^2 by removing the side portions by scraping.

The prepared TiO_2 photoanode was treated with UV−ozone for 30 min and heated to 80 °C. After that, the TiO_2 film was immersed in various dye solutions at room temperature for 24 h, each at a concentration of 3×10^{-4} M. N719 (Solaronix S.A., Aubonne, Switzerland) and D149 (Mitsubishi Paper Mills, Japan) were dissolved in a mixing solvent of ACN and tBA (volume ratio of 1:1) as a standard dye solution. Solutions of 3×10^{-4} M 5c dye [23] and 3×10^{-4} M SQ2 dye [24] (Luminescence Technology Corp, Taiwan) were individually prepared in a mixing solvent of ACN, tBA and DMSO (volume ratio of 3.5:3.5:3). The cocktail dye solutions with different volumetric ratios of 2/8, 4/6, 6/4 and 8/2 (SQ2/5c) were prepared by directly mixing different volumes of the individual dye solutions for the co-sensitization. The thus prepared TiO_2/dye electrode was placed on a platinum-sputtered FTO glass electrode, keeping the two electrodes separated by a 25 μm-thick Surlyn® layer (SX1170−25, Solaronix S.A., Aubonne, Switzerland). The two electrodes were then sealed by heating.

A mixture of 0.1 M LiI, 0.6 M DMPII, 0.05 M I_2, and 0.5 M TBP in MPN/ACN (volume ratio of 1:1) was used as the electrolyte. For the binary ionic liquid electrolyte, in the discussion of the long-term stability, 0.2 M I_2 and 0.5 M TBP were added in a mixture of two ionic liquids, PMII and $EMIBF_4$ (*v*/*v* = 65/35). The electrolyte was then injected into the gap between the electrodes by capillarity; the electrolyte-injecting hole was previously made in the counter electrode with a drilling machine, and the hole was sealed with hot−melt glue after the injection of the electrolyte.

2.4. Instrumentation and measurements

Surface of the DSSC was illuminated by a class-A quality solar simulator (XES-301S, AM 1.5G, San−Ei Electric Co., Ltd.). Incident light intensity (100 mW cm^{-2}) was calibrated with a standard Si Cell (Oriel Instrument, model 91105). The photocurrent density-voltage curves of the DSSCs were obtained with a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco-Chemie, the Netherlands). To obtain UV-absorption spectra, dye molecules were coated on the TiO_2 films and the corresponding spectra were obtained using a UV−visible spectrophotometer (UV−VIS−NIR, V670, Jasco Co., Japan) equipped with a total integrating sphere. Electrochemical impedance spectra (EIS) were obtained by the above−mentioned potentiostat/galvanostat, equipped with an FRA2 module, under a constant light illumination of 100 mW cm^{-2}. The frequency range explored was 10 mHz−65 kHz. The applied bias voltage was set at the open−circuit voltage of the DSSC, between the counter electrode and the FTO−TiO_2-dye working electrode, starting from the short-circuit condition; the corresponding ac amplitude was 10 mV. The impedance spectra were analyzed using an equivalent circuit model [27,28]. The incident photon-to-current conversion efficiency (IPCE) curves were obtained at the short-circuit condition. The light source was a class-A quality solar simulator (PEC−L11, AM 1.5G, Peccell Technologies, Inc.); light was focused through a monochromator (Oriel Instrument, model 74100) onto the photovoltaic cell. The monochromator was incremented through the visible spectrum to generate the IPCE (λ), as defined below,

$$IPCE(\lambda) = 1240(J_{SC}/\lambda\varphi) \tag{1}$$

where λ is the wavelength, J_{SC} is the short-circuit photocurrent density (mA cm^{-2}) recorded with a potentiostat/galvanostat, and φ is the incident radiative flux (W m^{-2}) measured with an optical detector (Oriel Instrument, model 71580) and a power meter (Oriel Instrument, model 70310).Eq. (1) is used to obtain the IPCE values.
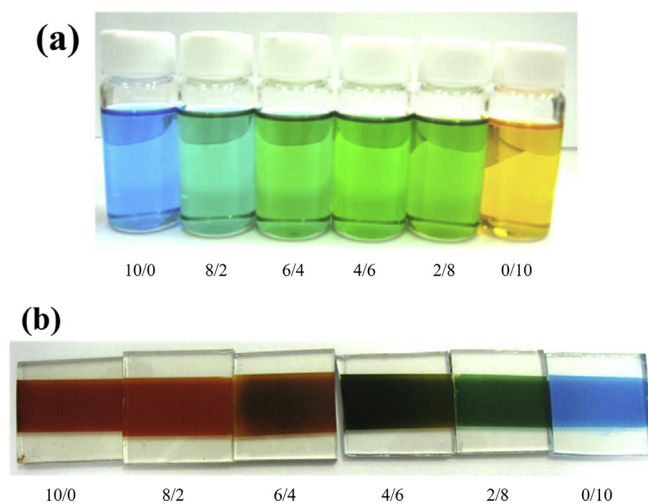

Fig. 1. Pictures of the (a) different cocktail dye solutions and (b) co-sensitized TiO_2 films with different cocktail dye solutions.

3. Results and discussions

3.1. Absorption spectra of the solutions and TiO₂ thin films with co-sensitized strategy

At the beginning of the co-sensitization work, we mixed the solutions of SQ2 and 5c at different molar ratios of SQ2/5c = 10/0, 8/2, 6/4, 4/6, 2/8, and 0/10. Fig. 1 shows the appearances and colors of the solutions and the TiO₂ photoanodes in different co-sensitizing conditions. As we can see, the colors for the solutions of SQ2 and 5c are blue and red, respectively. The colors for the thin films of SQ2 and 5c are consistent with those of their solutions. Both the solutions and thin films show a tendency of gradual color change when the portion of the 5c dye changes gradually. However, unlike the solutions, the co-sensitized photoanodes show much darker colors than the solutions when the molar ratios of SQ2 and 5c equal to 8/2, 6/4, 4/6, and 2/8. This phenomenon can be explained by different orientations of the dye molecules on the thin film [14]. The absorption spectra of the dye solutions and their sensitized TiO₂ thin films are shown in Fig. 2(a) and Fig. 2(b), respectively. The absorption spectra of the commercial N719 and D149 dye solutions and their sensitized thin films are also provided in Figure 2(c) and Figure 2(d), respectively. According to Fig. 2(a), we can see that the SQ2 and 5c dyes have obvious absorption wavelengths around 550–700 nm and 300–500 nm, respectively. Therefore, the absorption spectra are much broader for the co-sensitizers with the reference of the individual dyes. The results of these absorption spectra can be seen in Fig. 1 because the solutions and thin films with a darker color have a wider and a more intense absorption curve. Furthermore, the co-sensitized thin films can absorb more photons than the commercial D149 dye thin film and nearly equals to the absorption effect of the N719 thin films. It is expected that a better DSSC performance can be achieved based on the proposed co-sensitizers due to the improvements in the absorption spectra.

3.2. Photovoltaic performance of dye-sensitized solar cells with co-sensitized strategy

Fig. 3(a) and Fig. 3(b) presents the photovoltaic performance of the DSSCs sensitized by N719, D149, and the co-sensitizers in different conditions. Table 2 gives the corresponding cell performance parameters obtained from Fig. 3. According to Table 2 and Fig. 3, the co-sensitizing strategy is proved effective enough to give higher η values to the DSSCs. All of the DSSCs with the co-sensitization of SQ2/5c have better performance compared to the individual dyes, i.e., 3.98% and 5.33% for the cells with SQ2 and 5c dye, respectively. The improvements in the efficiencies are mainly due to the enhancement of the J_{SC} values, which are highly related to the range and the intensity of the absorption spectrum. The DSSCs reaches the highest η value of 6.24%, where the molar ratio equals to 4/6 (SQ2/5c). The V_{OC}, J_{SC} and FF values are obtained as 0.61 V, 17.86 mA cm^{-2}, and 0.57, respectively. According to Figure 3(a) and Figure 3(b), we can see the performance of the DSSC in the best co-sensitization condition (SQ2/5c = 4/6) is better than the organic-based D149 dye. However, the DSSC with N719 still performs better than the co-sensitized DSSC. Table 2 reveals that the DSSC with N719 dye achieves a higher cell efficiency because it offers a higher V_{OC} value (0.72 V) as compared to that of the co-sensitized ones (0.61 V). This is due to the molecular structure of N719, which leads to the MLCT effect [15] that impedes the charge recombination at the dye and TiO₂ interface, thus providing a higher V_{OC} value.

3.3. Incident photon-to-current conversion efficiency analyses for DSSCs

Fig. 4 illustrates the incident photon-to-current efficiency (IPCE) spectra of the DSSCs, which are sensitized by individual dyes SQ2, 5c, D149, N719 and the co-sensitizers at the best condition (SQ2/5c = 4/6). The maximum IPCE response of the individual SQ2 dye
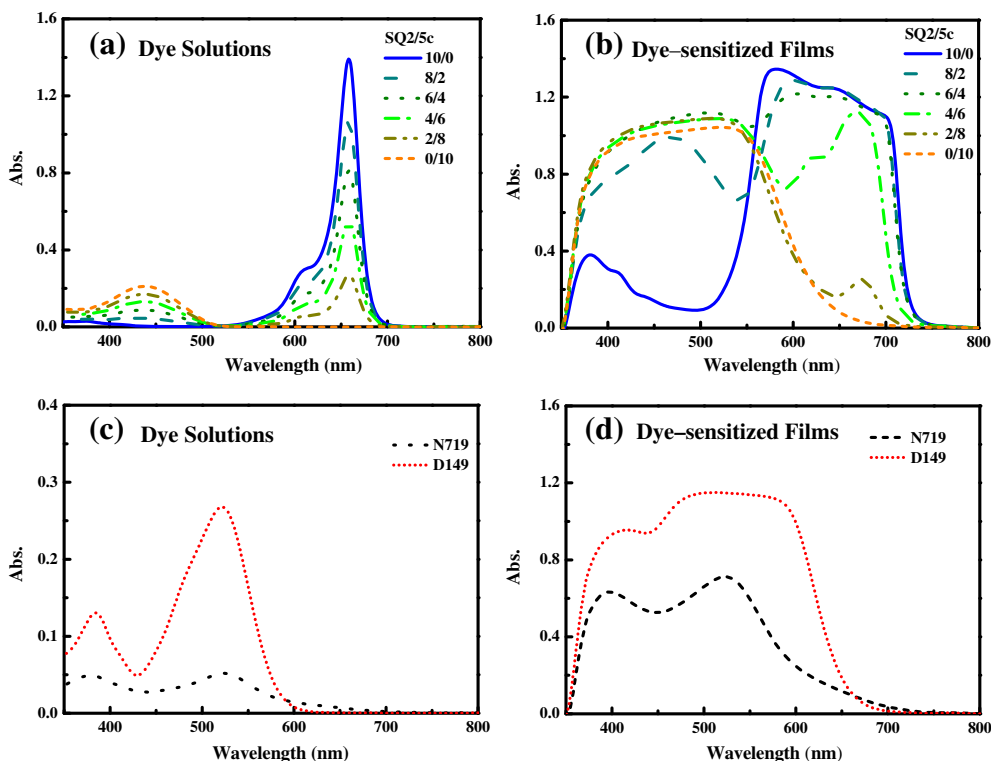

Fig. 2. UV–vis spectra of (a) cocktail dye solutions (SQ2/5c) with different volumetric ratios, (b) co-sensitized TiO₂ thin films sensitized with different cocktail dye solutions (SQ2/5c), (c) N719 and D149 dye solutions, and (d) TiO₂ films sensitized with N719 and D149 dye solution.
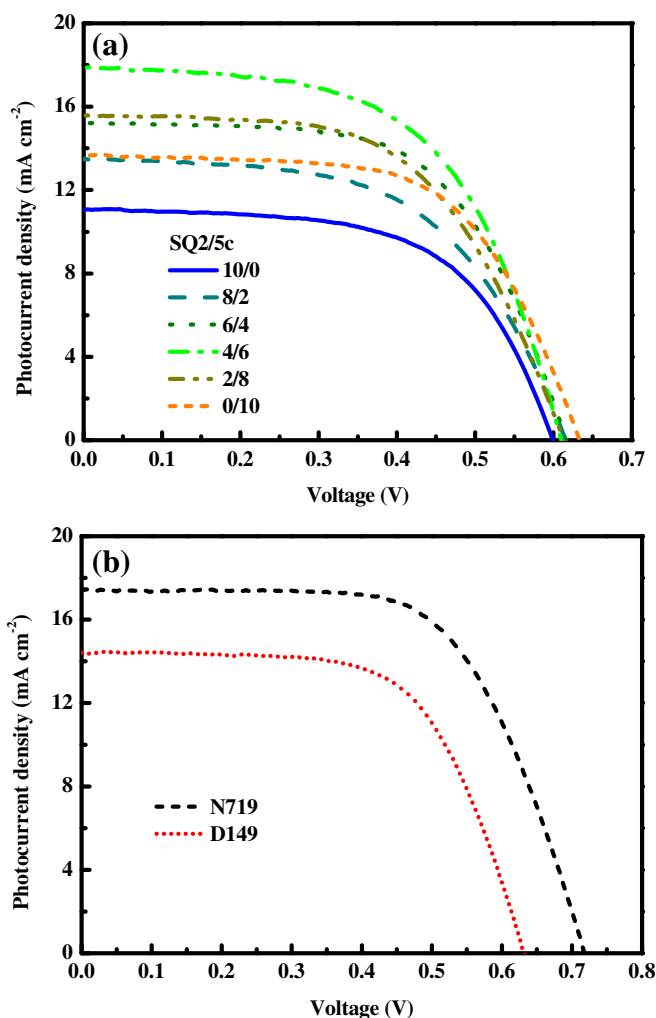
Fig. 3. Current density–voltage curves of the (a) co-sensitized DSSCs with different cocktail dye solutions (SQ2/5c), and (b) DSSCs sensitized with commercial N719 and D149 dyes, measured at 100 mW cm^{-2}.
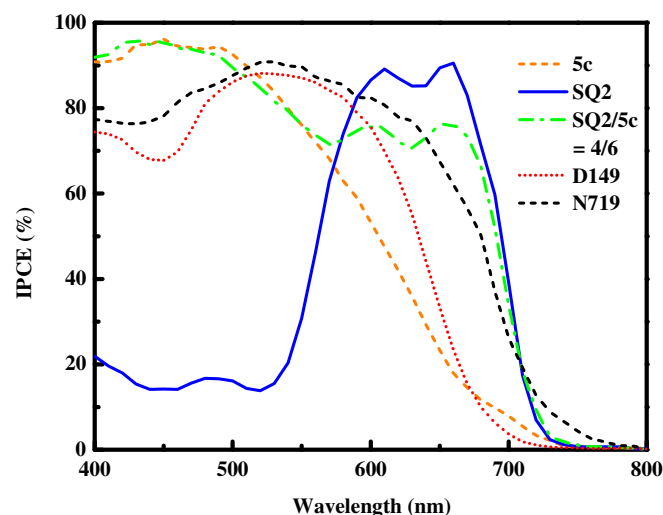

Fig. 4. The IPCE curves of the co-sensitized DSSCs with different cocktail dye solutions and of the DSSCs with commercial N719 and D149 dye solutions.

broader IPCE response, which accounts for the improvement in the J_{SC} and the photovoltaic efficiency of the DSSCs. The IPCE values obtained in Fig. 4 are consistent with the results presented in Table 2, namely, increasing J_{SC} with the co-sensitized strategy. The results obtained from the IPCE data support the co-sensitization effect (SQ2 and 5c), which leads complementary absorption, thus enhancing the J_{SC} and η of the DSSC.

3.4. Attempt to increase the cell performance with co-adsorbate

An attempt in further improving the DSSC performance was made by adding co-adsorbate chenodeoxycholic acid (CDCA) into the dye solutions. Dye aggregation, often noticed among the organic dye molecules, decreases the DSSC performance by impeding the ejected electron in the dye-TiO$_2$ interface to further inject into the TiO$_2$ band [13,29,30]. CDCA can prevent dye aggregation, at the same time improving the DSSC performance [13,31]. Fig. 5 and Table 3 are the photovoltaic performance and the corresponding parameters of the DSSCs sensitized by the co-

reaches 68% at 670 nm, while the responses of the 5c, D149, and N719 reach 72% at 455 nm, 65% at 525 nm, and 71% at 530 nm, respectively. According to Fig. 4, the IPCE of the DSSCs sensitized by SQ2, 5c, D149, and N719 range from 550 to 730 nm, 400−650 nm, 400−650 nm, and 400−780 nm in wavelength, respectively. A further comparison of the IPCE curves notes that neither the width nor the intensity of the SQ2 and 5c dye is comparable to that of the N719 dye. However, the co-sensitized IPCE curve is comparable with that of the cell containing N719 dye because the complementary behavior of the SQ2 and 5c dyes gives an enhanced and

Table 2
Photovoltaic parameters of the DSSCs with different cocktail dye solutions (SQ2/5c) and commercial dyes (D149 and N719).

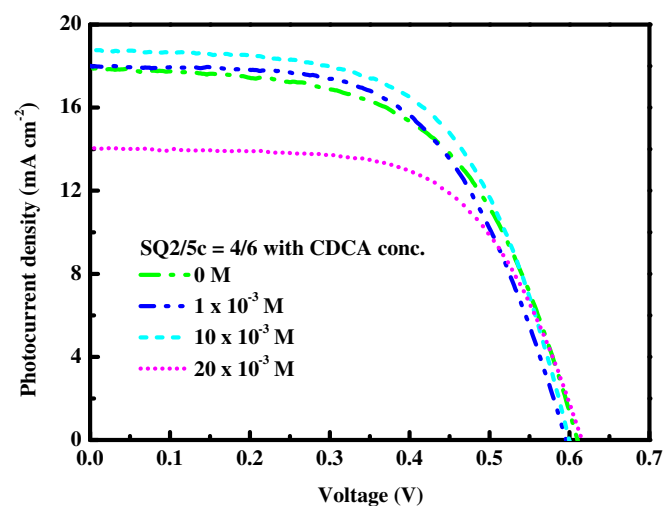| Samples	η (%)	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF
SQ2/5c = 10/0	3.98	11.05	0.60	0.60
SQ2/5c = 8/2	4.67	13.48	0.62	0.56
SQ2/5c = 6/4	5.69	15.20	0.61	0.61
SQ2/5c = 4/6	6.24	17.86	0.61	0.57
SQ2/5c = 2/8	5.47	15.59	0.61	0.57
SQ2/5c = 0/10	5.33	13.65	0.63	0.62
N719	7.97	17.43	0.72	0.64
D149	5.80	14.41	0.63	0.64

Fig. 5. The photocurrent density–voltage curves of the co-sensitized DSSCs with different concentrations of CDCA added in the SQ2/5c = 4/6 dye solution, measured at 100 mW cm^{-2}.

Table 3
Photovoltaic parameters of the DSSCs sensitized with commercial dyes (D149 and N719).

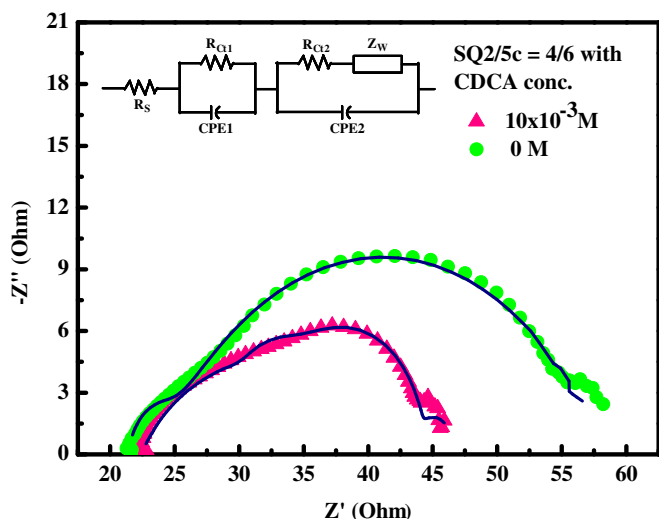| CDCA concentration (M)	η (%)	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	R_{ct1} (Ω)	R_{ct2} (Ω)	R_{diff} (Ω)
0	6.24	17.86	0.61	0.57	12.51	36.05	5.69
1×10^{-3}	6.27	18.01	0.60	0.58	–	–	–
10×10^{-3}	6.70	18.82	0.60	0.59	15.73	19.98	6.55
20×10^{-3}	5.20	13.64	0.60	0.63	–	–	–

Fig. 6. The EIS data of the DSSCs with different concentrations of CDCA added into the co-sensitized dye solution (SQ2/5c = 4/6), measured at 100 mW cm^{-2}. The fitting lines are obtained by using Z-View software.

sensitizers (SQ2/5c = 4/6) with different concentrations of CDCA. The η of the DSSC increases while the CDCA concentration increases and reaches the highest η of 6.70% at 1.0×10^{-3} M CDCA. However, the cell efficiency falls dramatically after the CDCA concentration reaches 1.0×10^{-3} M. Too high concentration of CDCA results in the competitive adsorption between CDCA and dye molecules, which impedes cell performance [31]. As the result, the decreased dye attachment on the TiO$_2$ thin film is responsible for the decrease in J_{SC}, leading to the drop in η.

3.5. Electrochemical impedance spectroscopy studies of the co-sensitized DSSCs with co-adsorbate

Electrochemical impedance spectroscopy (EIS) technique was used to study the charge transfer resistances of the cells. Fig. 6 shows the EIS data of the DSSCs sensitized in the condition with and without CDCA, and the equivalent circuit is shown inside Fig. 6. The fitting is done by using Z-View software and the fitting lines are included in Fig. 6 with the fitted resistances listed in the last three columns of Table 3. The ohmic serial resistance (R_s) in the equivalent circuit corresponds to the overall series resistance. In general, the impedance curve consists of three different semicircles. The first, second, and third semicircles corresponds to the charge transfer resistance at the counter electrode (R_{ct1}), at the TiO$_2$/dye/electrolyte interface (R_{ct2}) and to the Warburg diffusion process of I$^-$/I$_3^-$ in the electrolyte (R_{diff}), respectively. R_{diff} is virtually overlapped with R_{ct2} due to a short length for I$^-$ diffusion available with a thin spacer used (25 μm thick), and owing to the low viscosity of the solvents used in our electrolyte (viscosities of ACN and MPN are 0.37 cp and 1.60 cp, respectively). A significantly smaller R_{ct2} value of 19.98 Ω was obtained for the DSSC sensitized by a dye solution containing CDCA, as compared to that of the cell sensitized by a dye
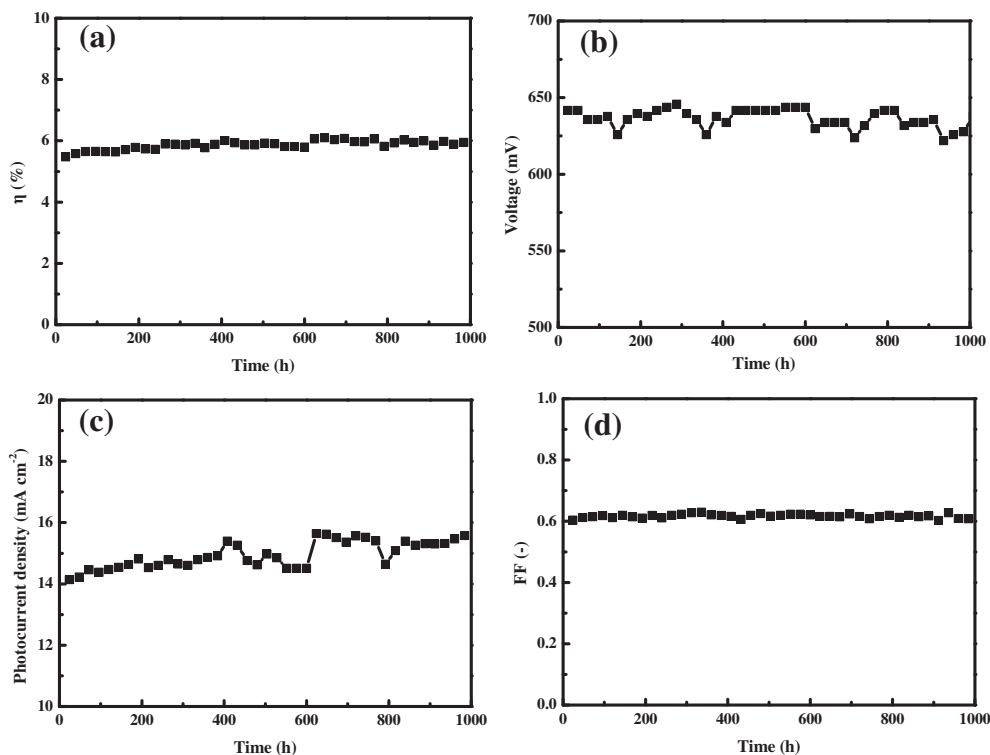

Fig. 7. The at-rest long-term stability data of the co-sensitized DSSCs (SQ2/5c = 4/6) with ionic liquid-based electrolyte.

solution without CDCA (36.05 Ω). The higher R_{ct2} of the DSSC without CDCA is due to the dye aggregation on the photoanode. The effectiveness of CDCA in preventing dye aggregation is supported by performing EIS analyses. It is generally accepted that CDCA can prevent dye aggregation and thereby decrease the charge transfer resistance (R_{ct2}) at the surface. The decrease of R_{ct2} with CDCA is consistent with the result presented in Fig. 5.

3.6. Durability of the co-sensitized DSSC with a binary-ionic liquid electrolyte

In order to investigate the durability of the co-sensitized photoanodes, which is sensitized with SQ2 and 5c dyes (SQ2/5c = 4/6), a binary-ionic liquid electrolyte was used for the corresponding DSSCs because the ionic liquids possess some advantages such as negligible vapor pressure, high thermal stability, wide electrochemical window, and high ionic conductivity [25,32–34]. Fig. 7 shows the at-rest long-term durability data of the co-sensitized DSSC. Cell efficiencies, V_{OC}, J_{SC}, and fill factor (FF) are measured every day after storing it in dark at room temperature. The co-sensitized DSSC shows uninterrupted photovoltaic parameters up to 1000 h.

4. Conclusion

A novel pyrenoimidazole-based organic dye, 5c, and a squaraine-based organic dye, SQ2, were used for the co-sensitization of the photoanodes of DSSCs. The absorption spectrum of the co-sensitized TiO$_2$ thin films becomes more intense and broader than the absorption spectra of the individual SQ2 and 5c dyes. As the result, the highest power conversion efficiency of 6.24% was reached for the DSSC sensitized with the co-sensitizers at a molar ratio of SQ2/5c = 4/6. Moreover, the cell efficiency of the DSSC with a molar ratio of SQ2/5c = 4/6 can be further improved to 6.70% with the addition of 10×10^{-3} M CDCA. The EIS analyses of the DSSCs with added CDCA shows that the charge transfer resistance (R_{ct2}) is lowered when the CDCA was added into dye solutions; this is consistent with the results of the photocurrents and the power conversion efficiencies. The IPCE curve showed a broadened and enhanced response when the two organic dyes were co-adsorbed on the TiO$_2$ film, which is consistent with the result of the absorption spectra. Moreover, the at-rest long-term stability of the DSSC with co-sensitized photoanode showed an unfailing efficiency up to 1000 h.

Acknowledgments

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